

NATIONAL BUREAU OF STANDARDS REPORT

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Progress Report
on
ADHESIVE RESTORATIVE MATERIALS



U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

NATIONAL BUREAU OF STANDARDS

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R. L. Bowen*, DDS, J. A. Barton**, DDS and A. L. Mullineaux***

* Associate Director, American Dental Assn. Research Unit,
National Bureau of Standards, Washington, D. C. 20234.

** Guest Worker, Dental Research Section, National Bureau of
Standards, Washington, D. C. 20234, LT-C from the U. S.
Air Force.

*** Research Associate, American Dental Assn. Research Unit,
National Bureau of Standards, Washington, D. C. 20234.

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U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

COMPOSITE RESTORATIVE MATERIALS

R. L. BOWEN, DDS* J. A. BARTON, JR., DDS†

and A. L. MULLINEAUX‡

DENTAL RESEARCH SECTION; NATIONAL BUREAU OF STANDARDS

WASHINGTON, D. C. 20234

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* Associate Director, American Dental Association Research Unit at the National Bureau of Standards.

† Guest Worker, Dental Research Section, National Bureau of Standards, Lieutenant Colonel, U. S. Air Force.

‡ Research Associate, American Dental Association Research Unit at the National Bureau of Standards.

COMPOSITE RESTORATIVE MATERIALS

I Historical Introduction

Although composite dental restorative materials are yet in their infancy, the roots of their development can be traced back through the scientific literature for many years. In 1843 a German chemist, Joseph Redtenbacher, reported a new acid to which he gave the name acrylic acid.¹ In the last part of the century, methacrylate esters and their polymers were discovered.¹ Probably before 1940, Schnebel had found that tertiary amines (such as Michler's ketone) would activate benzoyl peroxide to give self-hardening resins.² So far as can be determined, the first self-curing methyl methacrylate resin formulation for filling teeth was introduced in the United States in 1948.

There soon appeared on the market a number of direct filling resins, and many believed that these materials would be the answer to the shortcomings of the decades-old silicate cement. However, this idea was short-lived.³ These resin restorations discolored,⁴ tended to shrink away from the cavity walls,⁵ allowed the exchange of oral fluids around their margins,⁶ and were associated with pulpal inflammation⁷⁻⁹

and a high incidence of recurrent decay.¹⁰⁻¹¹ Furthermore, discrimination between decalcified dentin and the unreinforced direct filling resin was difficult because they were both radiolucent. For these and other reasons, a great many practitioners returned to the use of silicate cements.³

The shortcomings as well as the merits of silicate cements are well known. After nearly a hundred years¹² of development and use, these esthetic materials with good thermal and anticariogenic properties still have distinct disadvantages.³ Most obvious is the susceptibility to disintegration in a decay-like manner,¹³⁻¹⁵ typically after about four years in the mouth.^{3,14} Further description is given by Wilson elsewhere in this publication.

Because of the persistent need for a permanent, esthetic direct filling material, there were continued efforts to improve the methacrylate resins. An aluminum silicate filler (about 15%) was part of one methyl methacrylate monomer-polymer system.¹⁶ The use of fillers with the proper index of refraction and a low thermal expansion, and the develop-

ment of adhesion in the resin were advocated.¹⁷ Indeed, when inert fillers were incorporated into poly(methyl methacrylate), there was a reduction in the coefficient of thermal expansion and in the water sorption in proportion to the concentration of fillers.¹⁸ However, there was limited adhesive characteristics in these and certain other resins investigated.¹⁹

Epoxy resins,²⁰ developed early in the present century, had an annual production rate of about 20 million pounds by 1954. Certain formulations of these resins had intriguing properties including adhesive characteristics and the ability to harden at moderate temperatures with little shrinkage. These led numerous investigators to study epoxy resins as a binder for inorganic fillers.^{19,21} Primarily with indirect techniques, composite restorations were prepared using powdered fused silica and porcelain, bonded together with minor quantities of (heat-cured) epoxy resins. The good esthetics and other favorable properties of these composites encouraged the further investigation of this approach to dental restorative materials.²¹

However, attempts to develop composite materials using epoxy resins with various hardening agents for use in direct techniques met with numerous difficulties. Although initially adhesive to hard tooth tissues, the strengths of bonds between epoxy resins and enamel or dentin after prolonged exposure to water were disappointing.^{19, 21, 22}

II Early Composite Developments

The goal-directed research in which the composite dental restorative materials were developed was initiated at the National Bureau of Standards in 1956. After unsuccessful attempts to use various epoxy resins and hardening systems, a compromise between epoxy and methacrylate resins was conceived late in 1957.^{23, 24} The reaction sites (oxirane rings) of the epoxy molecule were replaced by methacrylate groups. This gave a hybrid molecule that polymerized through methacrylate groups.²⁵ It was suitable for use as a binder for reinforcing fillers because it was nonvolatile, had a relatively low polymerization shrinkage, and hardened rapidly under oral conditions when suitably formulated with an appropriate initiator system.

This dimethacrylate monomer (BIS-GMA) was synthesized by the reaction of bisphenol A and glycidyl methacrylate.²⁶ The same product is also produced by the reaction of the diglycidyl ether of bisphenol A and methacrylic acid.²⁵ Its structural formula²⁷ is shown in Figure 1.

Although BIS-GMA has been referred to as an epoxy resin, this is not the case; the original epoxy (oxirane) groups disappear during the synthesis and are, in effect, replaced by methacrylate groups. Unfortunately, this dimethacrylate monomer has also been called a polyester. The well-established term "polyester" should be restricted to the polycondensation products essentially of dicarboxylic acids with dihydroxy alcohols.²⁸

Since the coefficients of thermal expansion of organic polymers are many times higher than that of the dental hard tooth tissues,^{6,29} means for lowering this value were needed. Fillers¹⁷ incorporated into the resin could do this.¹⁸ Experimental composites prepared in 1953 utilized particles of fused silicon dioxide as a reinforcing filler because of

the extremely low coefficient of thermal expansion of vitreous silica.²¹ With the epoxy resin system, there was relatively good adhesion between the resin and the surfaces of these particles.

Later in the investigation, after the more-adhesive epoxy resins had been replaced by the less-adhesive dimethacrylate resins (BIS-GMA),²⁶ it became apparent that special means for attaining adhesive bonding between the resin matrix and the filler particle surfaces were required. At that time vinyl silane coupling agents appeared to be the most suitable means of improving this bonding.^{30, 31} The more reactive γ -methacryloxypropyl silane coupling agents^{32, 33} had not then become commercially available. A vinyl silane coupling agent applied to reinforcing filler gave composites that had about four times the tensile strength of composites utilizing the same filler without its being treated with the vinyl silane.³⁴ When the methacryloxypropyl silanes became available, their ability to promote adhesive bonding between the resin and glass was compared with that of vinyl silanes; the methacryloxypropyl silanes gave signi-

ificantly stronger and hydrolytically more-stable bonding than did the vinyl silanes.³⁵⁻³⁷

Since the strength and durability of the composites depended on the quality of the bonding between the organic matrix and the reinforcing filler particles, it was of utmost importance that the best coupling agents be used in the optimal manner. The coupling agent most widely used was γ -methacryloxypropyltrimethoxy silane, also known as 3-(trimethoxysilyl)propyl methacrylate. This organofunctional silane was hydrolyzed and condensed on the surfaces of the filler particles. It made the particles water repellent, reducing the water sorption of the composites; it also formed chemical bonds at the surface of the particles, connecting the organic polymer and the inorganic filler,³⁸ converting inert fillers to reinforcing fillers.³⁹

Although fused quartz or fused silica received a great deal of attention in experimental work,^{14, 21, 23, 24, 26, 34} many other filler materials were also investigated.^{16, 18, 19, 21, 31-34} These included the synthetic mineral β -eucryptite and closely

related materials,^{35, 40, 41} microcrystalline glasses,⁴² aluminosilicate glasses, barium-titanium glass, crystalline quartz and pyrogenic silica.³⁶ It has been widely held (although not universally accepted) that condensation between SiOH groups on the surfaces of these silica-containing fillers and SiOH groups of the hydrolyzed silane accounted for the bonding between the coupling agent of the filler and the filler particle itself. Copolymerization of the methacrylate groups of the silane with the methacrylate groups of the monomers comprising the organic continuous phase has been thought to complete the chemical linkage between the phases of the composites.³⁸

The BIS-GMA monomer was too viscous to be readily mixed with these fillers without first being thinned with some suitable monomer having a lower viscosity. Among others, methyl methacrylate and ethylene and tetraethylene glycol dimethacrylate, have been used for this purpose.^{23, 24}

As with antecedent methacrylates,¹⁶ stabilizers such as hydroquinone were first used to inhibit premature polymerization and give the necessary storage stability (shelf life)

to the BIS-GMA formulations.^{23, 26} On polymerization, less discoloration occurred with the use of the monomethyl ether of hydroquinone. Later, hydroquinone was replaced by BHT (butylated hydroxytoluene; 2,6-di-tert-butyl-4-methylphenol), a stabilizer that appeared to contribute no discoloring effects.⁴³

Other additives that contributed to color stability of the restorations were ultraviolet-absorbing compounds. While these may have contributed to the stability of the monomers during storage, their primary purpose was to reduce the amount of discoloration in the resin of the final composite material. Typical UV absorbers were 2-hydroxy-4-methoxy-benzophenone⁴³ and 2-(2'-hydroxy-5'-methylphenyl)benzotriazole.

Since most of the experimental work on composite materials utilized an amine-peroxide initiating system, another important component has been the amine accelerator. The most commonly used of these was N,N-dimethyl-p-toluidine (DMPT). This compound interacted with peroxides to produce free radicals which brought about the polymerization of the methacrylate monomer groups and thus the hardening of the resin binder of the composite. Investigations of factors that produce discoloration

in these materials led to the introduction of N,N-dimethyl-sym-m-xylylidine (DMSX; also known as DMDA), which not only gave less discoloration but also was a more effective accelerator than DMPT when compared on an equimolar basis.⁴³

In a composite material developed in Great Britain,⁴⁴ a long-chain mercaptan, together with an aliphatic peroxide, served as the hardening initiators.

Although other peroxides have been used,⁴⁴ benzoyl peroxide has been the one most used in composite restorative materials. It has been dispersed either in the reinforcing filler with the aid of a solvent that is removed by evaporation, or is dissolved in one of the monomeric liquids of the composite formulation.

Sulfinic acids or their derivatives were used in the initiator systems for experimental composite materials.¹⁴

III Some Properties of Experimental and Commercial Composites

Before proceeding with recent and current developments, perhaps it would be well to define "composite." For this discussion, the term "composite restorative material" refers

to a man-made, three dimensional combination of at least two chemically different materials with a distinct interface separating the components;³⁹ properties are thus obtained for the restoration of the form and function of defective teeth which could not be achieved by any of the components acting alone. Thus, the use of the term "composite" distinguishes the combination of inorganic aggregates bonded together with organic polymers from unreinforced direct filling resins and from silicate cements.

It is primarily the high proportion of reinforcing filler in composite restorative materials that yields properties different from those of direct filling resins. Most of the physical properties of composite restorative materials have been improved by the incorporation of a maximum amount of reinforcing filler together with a minimum amount of a binder of cross-linking polymerizable organic resin.

The "first generation" of commercial dental composite materials used BIS-GMA resin binder, described previously,

together with major portions of various particulate fillers and minor portions of various additives. Data that have been reported in the literature⁴⁵⁻⁶⁰ and more recently obtained^{61,62} show that composites have lower polymerization shrinkages and coefficients of thermal expansion, and higher compressive strengths and stiffnesses relative to unreinforced resins. Compared to silicate cements, the composites have lower solubilities and higher tensile strengths. More detailed data are given in Tables 1 and 2, including comparisons with dentin and enamel.^{24,63,68} The quantitative information presented in the tables is incomplete since the methods and conditions of measurement are not described; however, these data will serve to illustrate the ranges of values and order of magnitude to be expected with these materials.

The smoothness of the finished surface is comparable with that of silicate cements^{36,57,58} but inferior to that of unreinforced resins⁵² and most of the other restorative materials. The abrasion resistance of composite materials is superior to direct filling resins.^{36,47,48,51,56,58}

Similar to some other dental restorative materials, problems encountered in packaging and storage include volatility of some ingredients and premature gelation of resin components.³⁶

IV Current Research

Current research has the goal of making improvements on this "first generation" of composite materials now available to the dental practitioner. For example, there is a degree of pulpal irritation caused by some of these materials,^{69,70} and it has not yet been established which of the various ingredients contribute most to the inflammatory reactions of the dental pulp tissues. Other problems that have been encountered are incomplete color stability⁶² and resistance to staining, difficulties encountered in finishing and polishing, and lack of x-ray opacity.

The recent investigations at the National Bureau of Standards have led to new dimethacrylate monomers, reinforcing fillers, accelerators, stabilizers, and adhesion-promoting coupling agents that will, hopefully, lead to an

improved "second generation" of composite materials. For example, the BIS-GMA is not completely color stable and is too viscous for use without being thinned with a monomer of lower viscosity. Furthermore, it cannot be purified by distillation or by crystallization since it is inherently a mixture of non-volatile optical isomers. To overcome these problems, three dimethacrylate monomers were synthesized that can be prepared and purified separately by recrystallization.²⁷ These are the condensation products of 2-hydroxyethyl methacrylate with the acid chlorides of phthalic, isophthalic and terephthalic acids, respectively. Upon combining these three crystalline products, a ternary eutectic liquid mixture is formed that has a viscosity low enough to be used without the addition of any volatile ingredients. Preliminary tests show it to be non-toxic and non-irritating.²⁷

Numerous other monomers⁷¹⁻⁷⁵ are currently being synthesized and evaluated for use in dental composite materials.

The research effort to improve polymerization accelerators⁷⁶ has led to the successful synthesis of aromatic amines

having unusually high molecular weights⁷⁷ so as to minimize their solubilities in tissue fluids and thus their freedom to diffuse into the pulp or other tissues. The structure of these amines is based partly on the fact that the color stabilities of the composites have correlated better with the nature of the ring substituents than with the kind of nitrogen substituents in the amine accelerators.^{76,77}

Color stability is also profoundly affected by the characteristics of the stabilizers that are used. Significant advances are being made in the synthesis and utilization of stabilizers that are non-toxic and that do not cause discoloration of composites.^{43,76,77}

In the instance where there has been evidence of greater surface staining of composite restorations relative to the adjacent tooth enamel, it has not yet been determined to what extent this accretion of discolored material is due to inadequate hydrolytic stability of the adhesive bond between individual particles and the resin matrix, the chemical nature of the reinforcing filler materials, the chemical nature and degree of polymerization of the resin

formulations, the roughness of the surface after the restoration is finished,⁷⁸ or some combination of these factors. These factors are currently being studied.

Until recently, there has been little or no effort to prepare special materials to serve as reinforcing fillers for dental composite materials, rather, materials already available were selected for this application. However, the unique demands on this kind of composite material warrant the development and use of the most suitable fillers as well as other ingredients.

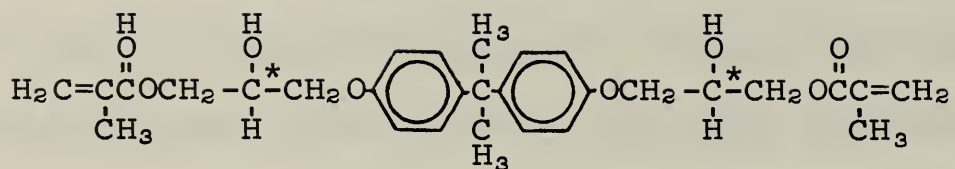
One experimental composite⁷⁹ contained a mixture of two reinforcing fillers: spherical particles of fused silica made up about two-thirds of the filler and smaller particles of an x-ray opaque glass made up about one-third of the filler. The smaller particles were composed of a special barium fluoride-containing glass that was developed for this purpose.⁸⁰ Radiopacity is desirable so that dentists can distinguish between the filling material and any carious dentin that underlies the filling.

The most recent investigations are involved with the preparation and evaluation of a single glass filler material containing silica and only enough barium to give the desired refractive index and x-ray opacity.⁸¹ Preliminary indications are that it will be suitable for converting into spherical particles utilizing conventional techniques while retaining the appropriate refractive index, and will have a low coefficient of thermal expansion. Chemically, the glass is formulated to have, at least in theory, hydrolytic stability in its bonding with the silane coupling agents.

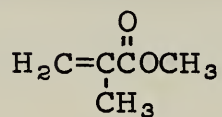
Since these composite materials are not intrinsically adhesive to the prepared tooth surface, special coupling agents have been developed which improve bonding between such composite filler materials and dentin and enamel. The chemical design of these special coupling agents was based on empirical observations of the types of groups that could displace water from the surfaces of powdered human enamel and dentin, thereby making the surface organophilic rather than hydrophilic.⁸²

One of the coupling agents, NPG-GMA (the reaction product of N-phenylglycine and glycidyl methacrylate), has two functions in the same molecule. One function is that of a chelate group that can form multiple bonds with calcium in the tooth surface. The other function is that of a methacrylate group, which can copolymerize with the hardening organic matrix of the composite material.⁸³ A solution of the coupling agent placed on the prepared tooth surface with the excess solution being wiped away leaves an invisible film. Following this, the freshly mixed (but not yet hardened) composite material is placed on top of this treated surface and the subsequent polymerization apparently includes the methacrylate groups of the coupling agent. The coupling agent has presumably also formed ionic and coordinate bonds with the tooth surface. Laboratory data on tensile adhesion tests clearly demonstrate that the use of the coupling agent significantly improved the adhesion between composite materials and tooth surfaces.^{83, 84} Clinical evaluations are under way.⁷⁹

There is a rapidly-expanding wealth of experience and information regarding composite dental materials, not only of the kind described here, but also of a wide diversity of materials and techniques.⁸⁶ Composite restorative materials, when they have been developed to their best potentialities, should eventually provide the dental profession and the public with greatly improved restorations for anterior teeth.



BIS-GMA



MMA

FIG 1.—Structural formula of BIS-GMA. The asterisks indicate asymmetric carbon atoms that give rise to a number of stereoisomers. Methyl methacrylate (MMA) is shown for comparison.²⁷

TABLE 1

SOME PHYSICAL PROPERTIES OF ESTHETIC DIRECT-FILLING MATERIALS

	Hardening Time minutes	Polymerization Shrinkage % (by volume)	Water Sorption % (by weight)	Solubility and Disintegration % (by weight)
Experimental Composites	4 ⁽¹⁴⁾			
	3-8 ^(24, 26)			
	5-7 ⁽³⁴⁾	2 ⁽²³⁾	0.9 ⁽²⁶⁾	0.00-0.08 ⁽²³⁾ 0.04 ⁽²⁶⁾
	7-10 ⁽⁴¹⁾	2.7-2.8 ⁽²⁶⁾	0.30-0.35 ⁽⁶²⁾	0.15-0.22 ⁽⁶¹⁾
	5 ⁽⁶¹⁾ 3.5-5 ⁽⁶²⁾			
Commercial Composites	3-4 ⁽⁵⁰⁾		0.78-2.46 ⁽⁵³⁾	
	1.5-4.5 ⁽⁵²⁾		1.60-3.68 ⁽⁵⁶⁾	0.01-0.08 ⁽⁵³⁾
	1-1.5 ⁽⁵⁵⁾	1.2-1.5 ⁽⁵²⁾	0.8-1.6 ⁽⁵⁷⁾	0.12-0.16 ⁽⁶²⁾
	2.5-5 ⁽⁵⁹⁾		1.12 ⁽⁶²⁾	
	3-3.5 ⁽⁶¹⁾			
Silicate Cements	4-6 ⁽¹⁴⁾	2 ⁽⁵⁾		0.4-1.1 ⁽¹⁴⁾
	4 ⁽³⁴⁾	3.3 ⁽²⁶⁾	--	0.4-1.3 ⁽²⁶⁾
		1.3 ⁽⁶⁰⁾		
Unreinforced Resin	6 ⁽¹⁴⁾	6-8 ⁽⁵⁾		
	6 ⁽³⁴⁾	6.2 ⁽²⁶⁾		
	3-3.5 ⁽⁵⁰⁾		[1.0-1.5 ⁽⁵⁾]*	[0.10 ⁽²⁶⁾] [†]
	4 ⁽⁵²⁾		[2.1 ⁽²⁶⁾] [†]	0.1 ⁽⁶⁰⁾
	2-4 ⁽⁵⁹⁾			

* Volumetric expansion

† Self-curing denture base resins

TABLE 2

SOME PHYSICAL PROPERTIES OF ESTHETIC DIRECT-FILLING MATERIALS,
DENTIN AND ENAMEL

	Tensile Strength psi*	Compressive Strength psi	Modulus of Elasticity psi x 10 ⁶	Coefficient of Linear Thermal Expansion ppm/°C	Indentation Resistance and Recovery	
					Indentation µm†	Recovery %
Experimental Composites	3,700-5,400 ⁽²⁴⁾	27,700 ⁽¹⁴⁾		26:35-45°C ⁽¹⁴⁾		
	4,000 ⁽²⁶⁾	23,000 ^(23,26)	1.4 ⁽¹⁴⁾	24:30-40°C ⁽²³⁾	55 ⁽²⁶⁾	77 ⁽²⁶⁾
	2,000-4,700 ⁽³⁴⁾	9,600-27,700 ⁽³⁴⁾	1.6 ⁽²⁴⁾	22:30-40°C ⁽²⁶⁾	58-96 ⁽³⁴⁾	56-72 ⁽³⁴⁾
	5,400-7,100 ⁽⁴¹⁾	12,000 ⁽⁴¹⁾	1.2-1.7 ⁽³⁴⁾	18,19,26:28-46°C ⁽³⁴⁾	50-70 ⁽⁶¹⁾	69-74 ⁽⁶¹⁾
	6,000-7,700 ⁽⁴⁵⁾	12,200-18,600 ⁽⁴⁵⁾	0.7-2.6 ⁽⁶¹⁾	19-39: 0-60°C ⁽⁴¹⁾	60-64 ⁽⁶²⁾	67-70 ⁽⁶²⁾
	3,700-6,000 ⁽⁶¹⁾	23,600-31,200 ⁽⁶¹⁾		30:24-58°C ⁽⁶¹⁾		
		26,000-27,000 ⁽⁶²⁾		31.5-35.7:25-49°C ⁽⁶²⁾		
Commercial composites†	2,000-5,900 ⁽⁵²⁾	17,400-29,000 ⁽⁵²⁾		27-41:24-88°C ⁽⁵²⁾		
	1,800-8,500 ⁽⁵⁷⁾	20,200-33,200 ⁽⁵³⁾	0.78-1.62 ⁽⁵²⁾	22-44:21-49°C ⁽⁵³⁾	65-97 ⁽⁵²⁾	62-70 ⁽⁵²⁾
	2,000-5,900 ⁽⁶²⁾	15,900-35,000 ⁽⁵⁷⁾	0.75-1.25 ⁽⁵³⁾	27-35:25-45°C ⁽⁵⁶⁾	50-90 ⁽⁶²⁾	48-72 ⁽⁶²⁾
		18,000-28,000 ⁽⁵⁸⁾	1.3-2.2 ⁽⁶²⁾	20-50: 0-60°C ⁽⁵⁷⁾		
		26,800-33,700 ⁽⁶²⁾		30-45:20-50°C ⁽⁵⁹⁾		
				31-41:30-55°C ⁽⁶²⁾		
Silicate Cements	440-1,010 ⁽²⁴⁾	24,300-30,000 ⁽¹⁴⁾	3.1 ⁽²⁴⁾			
	930 ⁽³⁴⁾	24,600-31,000 ⁽³⁴⁾	2.4 ⁽⁶⁵⁾	7.6:20-50°C ⁽⁶⁷⁾	40 ⁽²⁶⁾	83 ⁽²⁶⁾
		23,000 ⁽⁶⁶⁾	3.2-3.6 ⁽⁶⁶⁾			
Unreinforced Resin	3,800-5,100 ⁽²⁴⁾	12,100 ⁽¹⁴⁾	0.3 ⁽¹⁴⁾			
	3,300 ⁽⁵²⁾	10,700 ⁽²⁶⁾	0.26 ⁽²⁴⁾	100:35-35°C ^(14,34)	125 ⁽³⁴⁾	73 ⁽³⁴⁾
	3,100 ⁽³⁴⁾	11,000 ⁽⁶⁵⁾	0.34 ⁽⁵²⁾	92:24-88°C ⁽⁵²⁾	113 ⁽⁶²⁾	74 ⁽⁶²⁾
			0.27 ⁽⁶⁵⁾		95-115 ⁽⁶⁸⁾	60-80 ⁽⁶⁸⁾
			0.27 ⁽⁶⁸⁾			
Dentin			2.8 ⁽²⁴⁾			
		43,100 ⁽⁶³⁾	2.8 ⁽²⁶⁾	8:20-50°C ⁽⁶⁷⁾		
	7,500 ⁽²⁴⁾	50,400 ⁽⁶⁴⁾	2.4-2.7 ⁽⁶³⁾	7:25-55°C ⁽⁶²⁾	46 ⁽²⁶⁾	85 ⁽²⁶⁾
		31,500-44,200 ⁽⁶⁵⁾	2.2 ⁽⁶⁴⁾			
			1.1-2.0 ⁽⁶⁵⁾			

TABLE 2 (continued)

	Tensile Strength psi*	Compressive Strength psi	Modulus of Elasticity psi x 10 ⁶	Coefficient of Linear Thermal Expansion ppm/°C	Indentation Resistance and Recovery	
					Indentation μm†	Recovery %
Enamel	1,500 ⁽²⁴⁾	19,400-40,200 ⁽⁶⁴⁾ 13,700-41,800 ⁽⁶⁵⁾ 53,900-55,700 ⁽⁶⁶⁾	1.8-8.2 ⁽⁶⁴⁾ 1.4-9.1 ⁽⁶⁵⁾ 11-12 ⁽⁶⁶⁾	12:25-55°C ⁽⁶³⁾	33 ⁽²⁶⁾	86 ⁽²⁶⁾

* To convert psi (pounds per square inch) to MN/m² (meganeutons per square meter) multiply by 6,895 x 10⁻⁶

† Micrometers (microns)

Not all products are represented in each range of values shown

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